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## ***Interactive comment on “Natural iron enrichment around the Antarctic Peninsula in the Southern Ocean” by M. V. Ardelan et al.***

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Journal: BG Title: Natural iron enrichment around the Antarctic Peninsula in the Southern Ocean Author(s): M. V. Ardelan, O. Holm-Hansen, C. D. Hewes, C. S. Reiss, N. S. Silva, H. Dulaiova, E. Steinnes, and E. Sakshaug MS No.: bg-2009-106 Special Issue: Iron biogeochemistry across marine systems at changing times

Reply to Reviewers Comments:

We thank to the editor and both reviewers for taking time to read our paper and for their constructive comments. We have now made some change the manuscript to make it publishable in Biogeosciences

In the following, we list our responses to each of the referee's comments.

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1- English of the MS has been improved.

2- Regarding the comment on the use of NASS 5, we agree with reviewer that NASS 5 is not appropriate for open ocean iron research. During the analysis of our 2006 samples, NASS 5 was the only available certified seawater. We were aware of relatively high concentration of Fe in NASS 5; therefore, we prepared a set of spike solutions (Spike A) with 0.5, 1, and 1.5 nM Fe concentration. In the previous form of the MS, the result of the Fe determination in these spike solutions have been given together as a total recovery and % rsd but now we are giving the results of the tests of these spikes separately in the Table 1. For our samples from 2007-2008 cruises and future works we ordered SAFE from University of California Santa Cruz, and they are now available but it s too late to run SAFE for our 2006 data.

3- Line 2, 7483: We add the diffusion of iron as an additional iron sources

4- Line 6, 7485: “what are optical density measurements when applying to chlorophyll measurements.”

the section of “.....and also with the concentration determined by optical density measurements.” has been changed to “.....and also with with concentration determined by spectrophotometric readings using the optical density values for Chl-a as published by Jeffrey and Humphrey (1975).”

And “ Jeffrey, S.W., and G.F. Humphrey.: New spectrophotometric equations for determining chlorophylls a, b, c1 and c2 in higher plants, algae and natural phytoplankton. Biochem. Physiol. Pflanzen, 167:191-194 1975” has been added in references list.

5- Line 10, 7485. “In high chlorophyll waters, samples for nutrients should be filtered prior to freezing as the freezing process will result in cell breakage and hence intra-cellular nutrient release.”

Filtering process may also result in cell breakage and hence intra-cellular nutrient re-

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lease. Besides, risk of contamination may increase during the filtration. The WOCE Operation Manual WHP Office Report WHPO 91-1 (Nov 1994) pages 14 to 15, indicates that if there is a need to freeze the sample, this must be done as soon as possible, and it gives several instructions about how to proceed, but filtering the seawater was not mentioned. Many laboratories all over the world are following the freezing procedure and there is no consensus on the best preservation practice yet.

6- Line 23, 7486. "How was the buffer made, and make of chemicals"

The preparation of acetate buffer is a straightforward practice. It can be found elsewhere easily. The only relevant information regarding the preparation is the purity of ammonium acetate buffer. We have now explicitly mentioned that how ammonium acetate buffer has been made by using ultra pure  $\text{NH}_4\text{OH}$  (isothermally distilled) and ultra-pure acetic acid as : "Clean ammonium acetate buffer (1.4 M), was prepared by dilution of isothermally distilled ammonium solution with Milli Q water and slowly mixing with acetic acid (double distilled ultra pure, PPB/Teflon grade, Aldrich) under a fume hood."

7- Line 14, 7488. "The recovery test involving microwaving did not prove that dFe was quantitatively recovered following the microwave test. The NASS CRM was still not quite fully recovered following microwaving, and furthermore, the standard deviation (>10%) on the measurements was so large that a hard conclusion on this matter is not warranted."

Yes, we agree with reviewer #1 that NASS 5 has not been fully recovered, however, the spike solution in the coastal seawater was recovered. We remove "the hard conclusion" but both some cited literatures in the MS and our test suggest that microwaving helped to the decomposition of some organic ligands, hence increased the Chelex 100-lability iron in seawater.

8- Line 13, 7490. "I am not convinced that the higher beam attenuation at depth (100-350 m) for the three stations close to the shore could be attributed to suspended matter. There indeed appears to be an off-set in the readings for the deeper water. However

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this may well be due to a change in the electronic signal, as there appears to be a shift from 4.55 to 4.45 V. The conclusion is not properly supported.”

Please refer to Fig. 2 in Holm-Hansen and Hewes (2004. Deep chlorophyll-a maxima (DCMs) in Antarctic waters: I, Relationships between DCMs and the physical, chemical, and optical conditions in the upper water column. Polar Biol. 27: 699-710.) that shows profiles of various sensor and other data of 14-years of study in the AMLR survey area. This includes transmissometer data, which on average, is high in the upper 100 m and generally decays to background values by 200m, and corresponds with both fluorometric voltages and Chl concentrations. These patterns were generally observed during the AMLR survey of 2006. For all stations in Fig. 6 of our BG manuscript, chl fluorescence negatively corresponded with transmission volts in the upper 50-100 m, indicating that light attenuation was correlated with chl concentration. It was only below 100-200 m that there was not a correspondence between near shore and off shore profiles of transmissometer and fluorometer voltages. The probability that “change in the electronic signal” occurred just for the three shallow stations and only below 100-200 m is extremely unlikely, with the most likely explanation being that these data are real and that the increase in beam attenuation (i.e., lower voltages) at depth (100-350 m) is the result of re-suspension of particulate matter from the bottom sediments.

9- “Figure 8 is totally unclear to me. No TaLFe/DFe ratio is shown here. There must be something wrong with the graph.”

Fig 8 was drawn for estimation of the iron transport from near-shore to open ocean when the main current is parallel to the coast. For this purpose, we calculated “scale length” of the DFe and TaLFe by using the data from the near-shore survey. The purpose of Fig 8 has been explained thoroughly in section 4.2 on page 14 and in the caption of the Fig 8. We could not understand why we should give TaLFe/DFe ratio related to Fig. 8?

10- “Fig. 10 a is not very helpful, it just shows many wiggles and curves”.

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Essential points of our MS include (i) the concentration of Fe in the various water masses and in depth profiles, and (ii) the water flow patterns that are important in transporting Fe from coastal to pelagic regions and also the importance of eddies. Fig. 10a shows the real directional flow of water in the upper mixed layer as determined by drifter buoys. These tracks show the real complexity in water flow patterns. Fig. 10b is a simplified version of the data shown in Fig. 10a, which is useful to indicate the general directional flow of surface water.

11- Line 11, 7492. "Exceptionally high biomass. Provide values."

Sentence in MS as submitted: "Our DFe data for the Bransfield Strait and the coastal zones are lower, probably because of consumption by phytoplankton, which had attained exceptionally high biomass during our cruise compared to previous years (Hewes et al., 2009)."

has been corrected: "Our DFe data for the Bransfield Strait and the coastal zones are lower, probably because of consumption by phytoplankton, which had attained exceptionally high biomass during 2006, having a mean UML maximum of 4.0 mg Chl-a m<sup>-3</sup>, compared with an 18-year mean of 1.3 mg Chl-a m<sup>-3</sup> (Hewes et al., 2009)"

12- Line 21, 7492. "Upper limit of iron solubility is also critically governed by the solubility of inorganic iron species in solution, and the stabilization of iron in solution by organic ligands and colloids. (Pollard 2007 reference is not appropriate here). In cold waters the solubility will be higher."

Correction has been done

13- Section 4.3. "This is a nice section, however its significance is somewhat limited because of the large errors involved in the estimations. The waters in the study region are very dynamic. Nutrient (incl. Fe) ratios in these waters will be subject to strong seasonal changes due to physical and biogeochemical processes and hence the use of ratios from observed depth profiles will have limited use. Furthermore, the authors

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use f-ratios for the study region from previous studies. Again, these numbers will have a large uncertainty as the conditions under which these ratio's were obtained will have been very different."

We are aware of the possible uncertainty and limitation of these estimations. We had already mentioned the limitation of our estimations regarding the dynamic conditions of the region (se lines 4-8 page 16) and uncertainties of the Fe:C estimations in general (lines 11-15, page 16 ). Nevertheless, our Fe:C estimations are still useful. An additional remark on possible source of uncertainty of our estimation has now been added.

14- Line 13, 7498. "The statement that the central scotia sea chl a levels are low and dFe must not reach this sea region is contradicted on lines 20-21."

"Water from the Scotia Sea also flows north....." was has been corrected as "Water from the Weddell Sea also flows north....."

15- Line 22-28, 7498. "The final sentences of the manuscript are not convincing. What are the major findings of this work. Clearly upwelling of Southern ocean deep waters cannot result in important Fe enrichment as the Fe:N ratio in the upwelling deep waters is too low to result in enhanced biomass as the Fe is rapidly stripped out."

The sentence in the submitted MS "Future studies, however, must consider other possible sources of Fe enrichment....." has been changed to;

In order to create a complete iron balance, future studies must consider testing and comparison other possible sources of Fe enrichment ...."

Since this is the discussion section we think that our concluding paragraph is appropriate

Reviewer #2

1- regarding the comment on NASS 5, please see the reply #2 for reviewer #1

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2- Abstract: p 7482, line 4: “when Fe concentrations are measured on acidified unfiltered samples, this fraction is more generally called “Total Dissolvable Fe (TDFe)” instead of Total acid-leachable Fe (TaLFe) (e.g. see Löscher et al., 1997).”

We believe that “Total acid leachable Fe” is more descriptive for the measured Fe forms which were dissolved under pH = 1.8. This fraction of Fe may not represent the “total dissolvable Fe” in the nature. This is an “operational” definition and it is best to use the name that describes the used operation (namely solubilization/leaching of iron by acidification).

3-Introduction: p 7482, line 23: “for the high Chla concentrations above the Kerguelen Plateau, the authors can also refer to Blain et al. (2007). They can also mention the Crozet plateau (Pollard et al., 2009).”

We have added these two references in the MS.

4- p 7483 line 1-2: “Conversely, elevated chl-a concentrations in coastal and plateau areas are thought to be the result of re-suspension of iron-rich sediments and subsequent upwelling: : :”. Advection of water masses is also an important process to transport over long distance iron, which can be available for phytoplankton (e.g. Lam and Bishop, 2008).

Our sentence “Conversely...upwelling” is correct and appropriate. The following sentence “Advection....(e.g., Lam and Bishop, 2008) is not appropriate for our MS.

5- p 7484, line 11: “replace 2.1.2. by 2.5.”

Corrected

6- p 7486, line 3: “replace ‘throught’ by ‘through’”. Line 4, replace “filteation” by “filtration”. p 7489, line 9: replace “tbe” by “the”

All corrections have been done.

7- p 7489, lines 17-20: “When the averages for temperature, chl-a, nitrate, phosphate,

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D<sub>Fe</sub>, and TaL<sub>Fe</sub> in the UML at the 16 stations are plotted against salinity (Fig. 5), the data for individual stations within each group (Table 2) are fairly close with each group distinct from the other groups.” I do not find this sentence very clear.

This sentence has been corrected as

“When the averages for temperature, chl-a, nitrate, phosphate, D<sub>Fe</sub>, and TaL<sub>Fe</sub> in the UML at the 16 stations are plotted against salinity (Fig. 5), the data for individual stations are fairly close to each other within each group (Table 2) , and each grouping generally separated from the other four groups.”

8- p 7490, lines 15-16: “Concentrations of TaL<sub>Fe</sub>, which belongs to in the particulate fraction increased more rapidly than concentrations of D<sub>Fe</sub> with increasing density”. Rewrite this sentence

Corrected as; Concentrations of TaL<sub>Fe</sub>, which are portions of the particulate fractions, increase more rapidly than concentrations of D<sub>Fe</sub> with increasing water density (Fig. 3).

9- p 7490, lines 16-20: “these results have already been described earlier.”

It has been removed.

10- p 7490, lines 18-20: “The ratio of TaL<sub>Fe</sub>/D<sub>Fe</sub> decreased from \_ 60 in shallow waters (90 m) close to shore to \_ 9.4 in deep water (1200 m) 50km from the shore (Fig. 8).” This is not what is shown on fig. 8.

The exact values of TaL<sub>Fe</sub>/D<sub>Fe</sub> are 59.3 and 9,4 in shallow waters (90 m) close to shore and in deep water (1200m ) 50 km from the shore, respectively. These ratio can be roughly calculated by using Fig. 8. But the main purpose of the Fig 8 was not to show the TaL<sub>Fe</sub>/D<sub>Fe</sub> ratios. Fig 8 was drawn to estimate “the scale length” for D<sub>Fe</sub> and TaL<sub>Fe</sub>. Please see the reply # 9 for reviewer #1 , and relevant section (4.2) in the MS for more information on Fig. 8.

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11- p 7495: “the authors here estimate the Fe:C ratio using two methods with nitrate but only one with phosphate. Why was the method  $\text{Fe}:\text{NO}_3$  not used with phosphate?”

We calculated also  $\Delta\text{Fe}/\Delta\text{P}$  ratios from the average values of UML and pycnoclines in both DP and BS. We thought that it was not necessary to add them in the current MS. Now It has been added as follows;

“For Bransfield Strait average P concentrations were  $\sim 2.1 \mu\text{M}$  and  $\sim 1.9 \mu\text{M}$  for the pycnocline and the UML, respectively. For the Drake Passage, average P concentrations were  $\sim 1.9 \mu\text{M}$  and  $\sim 1.6 \mu\text{M}$  for the pycnocline and the UML, respectively. From these values and by using similar equation as...Eqn.. for P,  $\Delta\text{Fe}:\Delta\text{P}$  are estimated to be  $2.5\pm 0.7$  and  $0.6\pm 0.2 \text{ nmol}:\mu\text{mol}$ , for Bransfield Strait and the Drake Passage, respectively. Redfield ratios provide  $\text{Fe}:\text{C} = 6 \pm 3 \mu\text{mol}:\text{mol}$  in the Drake Passage water and  $24 \pm 7 \mu\text{mol}:\text{mol}$  in Bransfield Strait when  $\text{C}:\text{P} = 106 \text{ mol}:\text{mol}$ . which are also close to  $\text{Fe}:\text{C}$  estimations based on the slopes of the regression between DFe and P (Fig 9b).”

12- p 7495 line 23: change “obtained” by “obtain”

13- Fig. 4: “without the  $\ln$  scale, it would be easier to check if the DFe and TaLFe profiles are oceanographically consistent or not.”

We understand the concern of reviewer #2, At the beginning, we plot all figs without using  $\ln$  scale but it become difficult to visually compare different groups of data, which are quite distinct. Therefore we preferred  $\ln$  scale to be able to see all the data together in different groups

Sincerely

M. V. Ardelan, O. Holm-Hansen, C. D. Hewes, C. S. Reiss, N. S. Silva, H. Dulaiova, E. Steinnes, and E. Sakshaug

Interactive comment on Biogeosciences Discuss., 6, 7481, 2009.

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